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Coordination chemistry in electrocatalysis

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Abstract: Superior electrocatalysts for the reduction of O_2 by four-electrons in one step have been prepared by coordinating ammine complexes of Ru(II) to the pyridine ligand sites in cobalt tetrakis(4-pyridyl) porphyrin. At least three coordinated Ru(II) centers appear to be required to obtain the four-electron reduction. When *fac*-$Ru(NH_3)_3(OH_2)_3^{2+}$ was used to ruthenate the porphyrin, a network structure was obtained in which both terminal and bridging ruthenium centers were present.

The catalysis of electrode reactions is often accomplished by preparing active sites on electrode surfaces that serve as "electrocatalysts". Most simple electrode processes, i.e., reactions which involve the transfer of a single electron without accompanying atom or ion transfer that leads to the making and/or breaking of chemical bonds, usually do not require or benefit from electrocatalysis. The rates of such simple electrode processes are often diffusion controlled. By contrast, electrode processes that involve the transfer of several electrons, usually accompanied by the breaking of old bonds and the creation of new ones, commonly proceed slowly or not at all in the absence of electrocatalysts. Such complex electrode processes often involve high energy intermediates that must be stabilized by interactions with suitable molecules or complexes if the electrode reactions are to proceed at reasonable rates. These intermediate-stabilizing species are the electrocatalysts.

Transition metal complexes with demonstrated activities as homogeneous catalysts can sometimes be utilized as electrocatalysts by attaching them to the surfaces of electrodes. An example of this strategy is provided by the catalysis of the electroreduction of O_2 at carbon or graphite electrodes in aqueous acid [1]. The reduction proceeds at unmodified graphite electrode surfaces but only at electrode potentials much more negative than the thermodynamically required values. In addition, the most common product of the reduction is H_2O_2 instead of the thermodynamically more favored product, H_2O. If cobalt porphyrins are introduced on the surface of graphite electrodes by, for example, irreversible adsorption, the electroreduction of O_2 is catalyzed

in the sense that it commences at much less negative potentials than are required at a bare graphite surface. However, the electrode process continues to produce only H_2O_2 as the reduction product. It is generally believed that cobalt porphyrins adsorbed on graphite serve as electrocatalysts for the reduction of O_2 by coordinating the O_2 molecule to the Co(II) center of the porphyrin. The coordinated O_2 is "activated" and accepts two electrons from the electrode more readily than does an uncoordinated O_2 molecule. In an attempt to induce the coordinated O_2 to accept four instead of two electrons, we have been exploring the use of modified cobalt porphyrins as electrocatalysts [1-6]. Our modified porphyrins contain substituents at the four *meso* positions of the porphyrin ring. The substituents selected are ligands to which transition metal complexes may be coordinated. By choosing complexes which undergo facile, one-electron changes in oxidation state, we hoped to achieve a rapid, four-electron, intramolecular electron transfer to O_2 molecules coordinated to the cobalt(II) centers of the modified porphyrin. Our first success was obtained with the tetraruthenated tetrapyridyl porphyrin shown in Fig. 1. At graphite electrodes coated with this porphyrin the four-electron electroreduction of O_2 to H_2O occurred while the unruthenated porphyrin produced only H_2O_2 as the reduction product [1, 2].

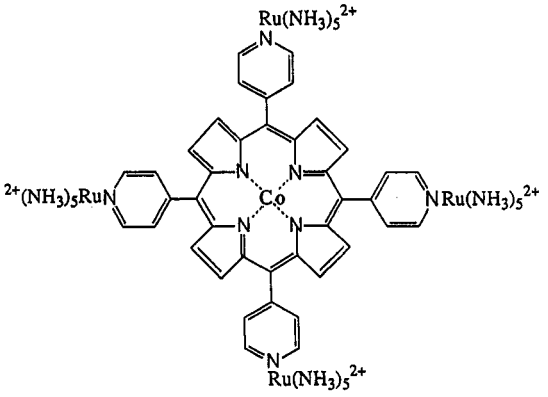

Fig. 1.
Tetraruthenated cobalt *meso*-tetrakis(4-pyridyl) porphyrin.

A set of cobalt porphyrins having all possible combinations of phenyl and pyridyl substituents in the *meso* position.

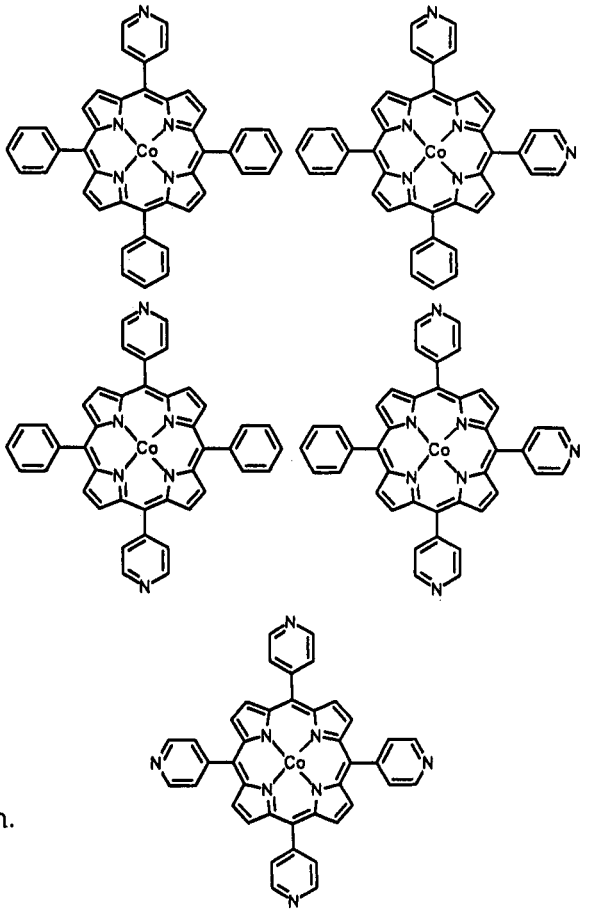

Fig. 2.

In subsequent experiments, sets of porphyrins containing various combinations of ligand sites appended to the porphyrin ring have been synthesized and examined as electrocatalysts for the reduction of O_2. For example, a set of cobalt porphyrins having mixtures of phenyl and pyridyl substituents is shown in Fig. 2. $Ru(NH_3)_5$ groups were coordinated to the pyridine ligands in all of the porphyrins in Figure 2 and the resulting molecules were tested as electrocatalysts for the reduction of O_2. The porphyrins that contained three or four coordinated $Ru(NH_3)_5^{2+}$ groups catalyzed the four-electron reduction of O_2 while the other three ruthenated porphyrins catalyzed only the two-electron reduction [3].

When the ruthenation of the tetrapyridyl cobalt porphyrin was carried out by reacting the porphyrin adsorbed on graphite electrodes with *fac*-$Ru(NH_3)_3(OH_2)_3^{2+}$ instead of $Ru(NH_3)_5OH_2^{2+}$, an apparently oligomeric coating was obtained in which both bridging and terminally coordinated Ru centers were present [5]. A possible structure for the coating, consistent with its electrochemical properties, is shown in Fig. 3. Such coatings catalyze the four-electron reduction of O_2 [5].

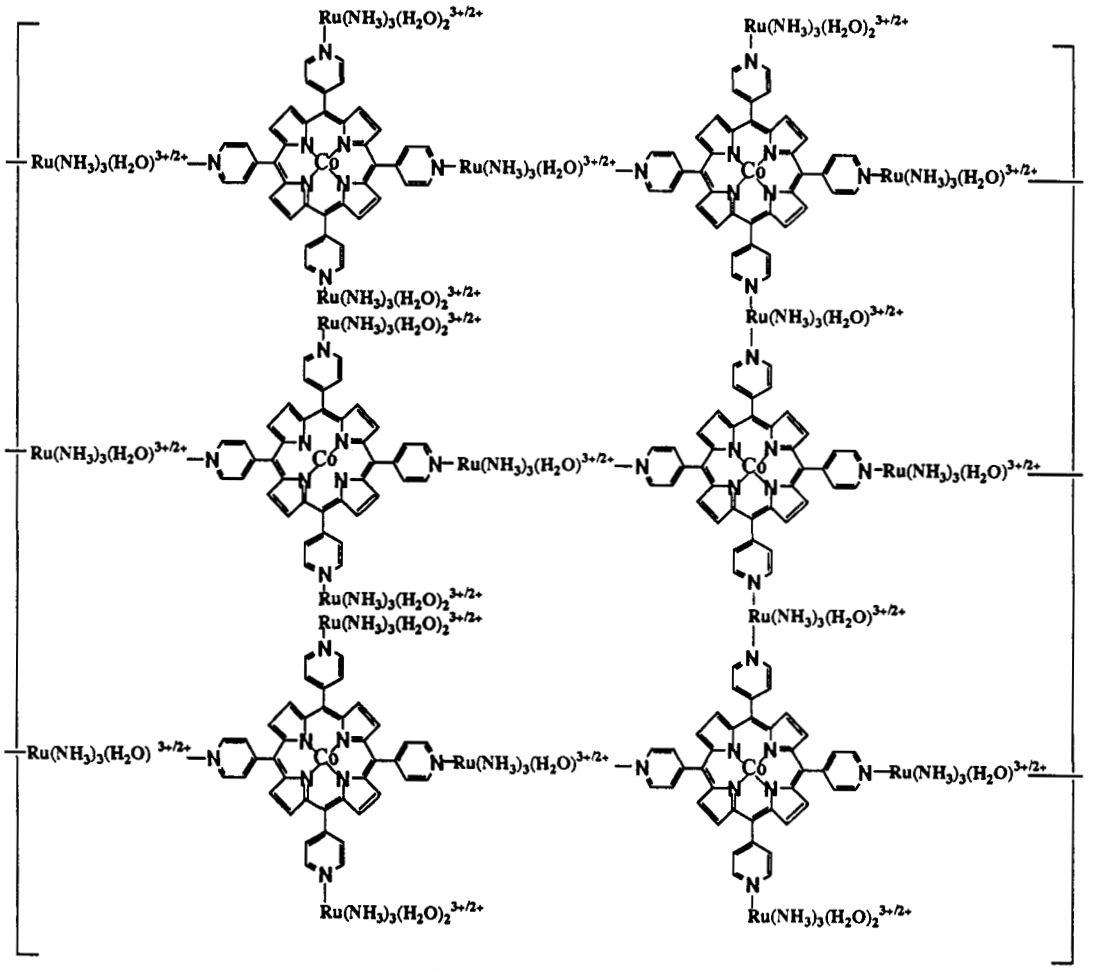

Fig. 3. A possible structure for a portion of the network of cobalt *meso*-tetrakis(4-pyridyl) porphyrins produced by ruthenation with *fac*-$Ru(NH_3)_3(OH_2)_3^{2+}$.

The mechanisms through which these ruthenated cobalt porphyrins operate as four-electron reduction catalysts is thought to depend upon back-bonding interactions between the Ru(II) centers and the porphyrin ring. These interactions are believed to affect the activation of the O-O bond of O_2 molecules that are coordinated to the Co(II) center in the porphyrin [3, 4]. Rapid, intramolecular electron transfer and cycling of the ruthenium centers between oxidation states do not appear to be essential features in the catalytic mechanism [3, 6].

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REFERENCES

1. C. Shi and F. C. Anson, *J. Am. Chem. Soc.*, **113**, 9564 (1991) and references cited therein.
2. C. Shi and F. C. Anson, *Inorg. Chem.*, **31**, 5078 (1992).
3. B. Steiger, C. Shi and F. C. Anson, *Inorg. Chem.*, **32**, 2107 (1993).
4. C. Shi and F. C. Anson, *Electrochim. Acta*, **39**, 1613 (1994).
5. C. Shi and F. C. Anson, *Inorg. Chim. Acta*, in press, 1994.
6. B. Steiger and F. C. Anson, submitted to *Inorg. Chem.* 1994.